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ELECTRIC-FIELD EFFECTS IN ESR SPECTRUM OF LOW-SPIN CENTER Ni^{3+} IN $KTaO_3$ CRYSTALS (PREPRINT)

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14. ABSTRACT

Electric-field effects in ESR spectrum of low-spin (S=1/2) tetragonal center Ni^{3+} was studied in $KTaO_3$ single crystals. Orientation of the centers as well as splitting of the resonance lines was found resulting from the external E-field interaction with the electric dipole moment of the center. The value of the dipole moment was determined to be p=103D=21.4 eÅ. An analysis of the experimental results allowed us to make a reasonable choice of microscopic models for two nickel centers in $KTaO_3$.

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Electric-field effects in ESR spectrum of low-spin center Ni^{3+} in $KTaO_3$ crystals.

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Electric-field effects in ESR spectrum of low-spin (S=1/2) tetragonal center Ni^{3+} was studied in $KTaO_3$ single crystals. Orientation of the centers as well as splitting of the resonance lines was found resulting from the external E-field interaction with the electric dipole moment of the center. The value of the dipole moment was determined to be p=103D=21.4 eÅ. An analysis of the experimental results allowed us to make a reasonable choice of microscopic models for two nickel centers in $KTaO_3$.

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1. Introduction

Iron-group impurities in $KTaO_3$ are known to enter substitutionally on either tantalum or potassium site. Besides, these 3-d ions can have different defects in a close proximity, thus forming a wide variety of defect centers in potassium tantalite.

In late sixties, two tetragonal Ni^{3+} centers were found in $KTaO_3$ [1]; recently we have observed a nickel center of orthorhombic symmetry [10]. Unlike two Fe^{3+} centers found in $KTaO_3$ [14], tetragonal Ni^{3+} centers can have two different spin values – low-spin (S=1/2) and high-spin (S=3/2) depending on the type of cation nickel substitutes for (Ta site has an octahedral surrounding whereas K site has an icosahedral surrounding).

However, the exact positions of each of the two centers remain unclear. Most likely, this problem can not be solved with the use of only Hund's rule, without knowledge of three characteristic energies: crystal field splitting of the levels 10Dq, spin-orbit coupling, and exchange interaction.

The origin of tetragonal distortion of the crystal field is another open question. The authors of [1] suggested a Jahn-Teller nature of tetragonal distortion, others believe it to be rather a neighboring oxygen vacancy [3], potassium vacancy [2], interstitial oxygen, or a noncentral position of nickel ion [2].

This paper presents the study of the electric-field effects in the ESR spectrum of the low-spin (S=1/2) center Ni^{3+} in $KTaO_3$. An analysis of the experimental results allowed us to choose a microscopic model for the center.

2. Experiment technique

The experiments were performed on the samples of potassium tantalate grown in the Laboratory of Crystal Growth of Osnabrück University, Germany. Rectangular samples with the edges aligned with <100> and measuring typically 0.9x4x6 mm were cut from a single-crystal boule. Aquadag-paste electrodes were deposited on 4x6-mm faces. The sample with electrodes was immersed in an insulating paste. This made it possible to apply a high voltage (up to 10 kV) across the sample, not only in liquid but also in gaseous nitrogen. The ESR spectra were measured on a modified 3-cm Radiopan SE/X2544 spectrometer with 100-kHz magnetic field modulation.

ESR signals from both low-spin (S=1/2) and high-spin (S=3/2) centers are observed in as-grown

$KTaO_3$ samples exposed to UV light at 78 K. Subsequent irradiation of the sample with red light increases concentration of high-spin centers and at the same time decreases that of low-spin centers.

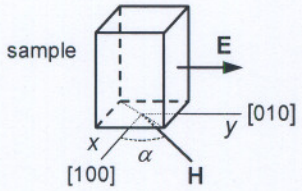

Fig. 1. Direction of the electric and magnetic fields

3. Linear dependence of line splitting on electric field

An external electric field up to 105 kV/cm was applied at liquid nitrogen temperature along one of the cubic axes of the $KTaO_3$ crystal (Fig.1). In this layout, for the centers with the axis parallel to x, an electric-field effect manifests itself in a partially resolved line splitting (Fig. 2).

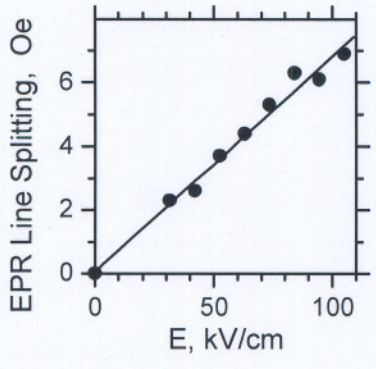

Fig. 2. Splitting in the external electric field of the ESR line of the low-spin-Ni^{3+} center oriented along *x*, E || y, E = 105 kV/cm, T = 78 K, ν = 9.4 GHz.. Circles –. the values extracted from the experiment as explained in the text, line – linear fit.

The splitting appears as soon as the field is applied, and there are no further changes in the splitting value or in the intensities of the components. This means that there are two states of the center, which are unresolved in the absence of the electric field.

At lower values of the applied field the effect is observed as a broadening of the line that initially has a width of 6.5 Oe. In order to extract the values of line splitting, we made a fit of the experimental line shape with the zero-field line split in two halves by a variable parameter. Fig. 2 shows the splitting parameter that gives the best match, which yields a linear dependence.

4. Alignment of Ni Centers in the Electric Field

Linearity of the electric-field effect in the ESR spectrum of the discussed center is evidence for a non-inversion symmetry in the site with substituent nickel. In other words, the discussed center must have an electric dipole moment.

To be oriented by an external electric field, the dipole center must have a possibility to undergo spontaneous (thermal) reorientations at the temperature of the experiment. These reorientations are not observed at T=78 K, but they are detectable at higher temperatures. A distinct alignment of nickel centers was observed between 120-130 K.

By varying a temperature within this range, we have determined a value of the electric dipole moment. The ratio of intensities of the lines related to differently oriented centers was measured in a two-step procedure:

a) an E-field was applied to the sample along one of the cubic axes at 120-130 K. In this temperature interval, the equilibrium between the centers aligned along and perpendicular to the direction of E-field is established rather quickly (2-3 minutes at 125 K).
b) Subsequently, the temperature was rapidly (in a 5-10 seconds) decreased to 100 K (the characteristic reorientation time at 100 K is about few days), the E-field was switched off, and ESR spectrum was recorded. Recording the spectra in zero E-field allows for the avoidance of a problem with line shape distortion by external field.

The ratio n_y/n_x, where n_y and n_x are intensities of the resonance lines of the Y and X centers (E-field was parallel to Y axis) was plotted in coordinates $\mathrm{arch}(n_y/n_x)$ *vs.* E/kT (Fig.3). The dependence appears linear with a good accuracy. The data on Fig. 3 were obtained by varying the external E-field from 0 to 74 kV/cm and the temperature from 122 to 130 K. The slope ratio of the line is equal to the electric dipole moment of the center **p**:

$$p = (21.4 \pm 2.0)\ e\text{Å} = (103 \pm 10)\ D$$

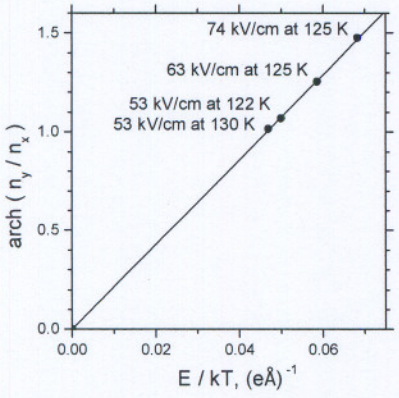

Fig. 3. arch(n_y/n_x) as a function of E/kT. The values were obtained from the measured ratios of the concentrations of the centers oriented along y and x axes at different temperatures and external fields.

5. Line splitting dependence on the orientation of electric and magnetic fields

Fig. 4 shows the angle dependence of resonance line splitting for the centers oriented along x axis, when electric field is *perpendicular* to the axis of the center ($\mathbf{E} \parallel y$) and the magnetic field rotates in the (*xz*) plane (Fig. 1). The splitting equals zero for the directions $\mathbf{H} \parallel x$, $\mathbf{H} \parallel y$, and $\mathbf{H} \parallel z$; it reaches a maximum when **H** lies in (*xz*) plane at ~45° to the *x*- axis.

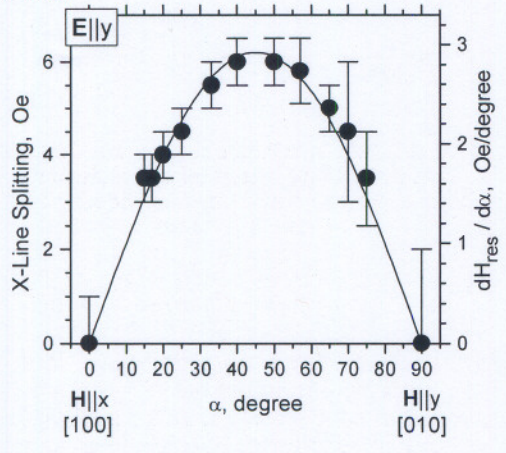

Fig. 4. Correlation between the angular dependence of the splitting in the electric field and that of the first derivative of the resonant magnetic field. Circles – splittings in the electric field (left axis), solid curve – first derivative of resonant magnetic field (right axis), the centers are oriented along *x*-axis, E = 105 kV/cm.

To the best of our knowledge, a similar manifestation of electric-field effect in ESR was observed only once [9] on the $Fe^{3+}{}_K$–O_i center (in potassium tantalite also).

It is explained as follows: in the electric field perpendicular to the axis of the center, the dipole center slightly rotates by a small angle. Consequently, the angle between the axis of the center and the direction of the magnetic field changes. In the layout shown in Fig.1 for the center with dipole moment along +x, this angle slightly decreases, whereas for the center with dipole moment along –x, it slightly increases; therefore, the shifts are opposite and the line splits. The value of the splitting must be directly correlated with the first derivative of the resonant magnetic field as a function of angle in this plane, which, indeed, takes place as one can see on Fig. 4.

In addition to the effect described in [9], we have observed also a splitting of the resonance lines (smaller in magnitude than one described above) for the centers *parallel* to the external electric field. Although we failed to obtain a presentable angle dependence δH(**H**) in this layout, the presence of the effect is beyond any doubts.

6. Discussion on the microscopic structure of the center

6.1 As noted in the introduction, two tetragonal ESR spectra are observed in $KTaO_3$:Ni and attributed to Ni^{3+} ions with different values of effective spin. To clarify the position of each of the two Ni^{3+} ions in the lattice of potassium tantalate we compared electric-field effects observed on Ni^{3+} ions with those found for Fe^{3+} in $KTaO_3$. As mentioned above, the main features of electric-field effect for Ni^{3+} centers perpendicular to E-field are similar to the results reported for Fe^{3+} ions in potassium site in $KTaO_3$ ($Fe^{3+}{}_K$–O_i) [9]. Authors of [9] suggested the mechanism for the effect to be a rotation of the dipole center, by a small angle, in the external electric field. It is important that the ionic radii of Ni^{3+} and Fe^{3+} ions are both much smaller than that of K^+ (~1.4 Å), which makes it easier for the centers to deviate in an external field. We believe this is a strong argument for the potassium site to be occupied by the low-spin nickel ion. On the other hand, the electric field does not split resonance lines in the ESR spectrum of the high-spin (S=3/2) Ni^{3+} center. Absence of the electric field effect was also reported for the $Fe^{3+}{}_{Ta}$ center, iron in the tantalum site, [13] and this justifies our assignment.

6.2 Another issue regarding the microscopic structure of nickel centers that remained unclear up to date is the origin of tetragonal symmetry of the crystal field. The linearity of the electric-field effect reported in this paper allows us to disregard the idea of Jahn-Teller nature of tetragonal distortion of the low-spin nickel center in potassium tantalite as given earlier [1].

Furthermore, the dipole moment of the center is very unlikely to arise from a noncentral position of the nickel ion because of a relatively large value of the dipole moment (p=21.4 eÅ). On the other hand, the value found for **p** differs by only 30% from that of the $Fe^{3+}{}_K$–O_i center in $KTaO_3$ [13]; the structure of the latter was reliably established in [14] by means of ENDOR. This allows us to suggest that the low-symmetry center of nickel has a similar structure, *i.e.* Ni^{3+} in potassium site next to an interstitial oxygen ($Ni^{3+}{}_K$–O_i).

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References

1. D.M. Hannon. Phys. Rev. **164**, 366 (1967).
2. Y. Akishige and K. Ohi. Jap. J. Appl. Phys. **19**, 1633 (1980).
3. M.M. Abraham, L.A. Boatner, D.N. Olson, U.T. Höchli. J. Chem. Phys. **61**, 2528 (1984).
4. D.M. Hannon. phys. status solidi B **43**, K21 (1971).
5. A.G. Badalyan, P.G. Baranov, D.V. Azamat, V.A. Trepakov, C.B. Azzoni, P. Galinetto, M.C. Mozzati, L. Jastrabik, J. Rosa. J. Phys.: Condens. Matter **14**, 6855 (2002).
6. S. A. Basun, L. S. Sochava, V. E. Bursian, H. Hesse, S. Kapphan, V. S. Vikhnin. Proc. of the XIII Internat. Conf. on Defects in Insulating Materials, Wake Forest University, USA, July 15-19, 1996, in Materials Science Forum, Trans Tech Publications, Switzerland **239-241**, 345 (1997).
7. S.A. Basun, V.E. Bursian, A.G. Razdobarin, L.S. Sochava. Physics of the Solid State **43**, 1059 (2001).
8. S.A. Basun, A.G. Razdobarin, L.S. Sochava, D.R. Evans. Physics of the Solid State **46**, 258 (2004).
9. I.N. Geifman, M.D. Glinchuk, B.K. Krulikovskii. Zh. Exp. Teor. Fiz. **75**, 1468 (1978).
10. L.S. Sochava, V.E. Bursian, A.G. Razdobarin, S.A. Basun, D.R. Evans, S.E. Kapphan. Physics of the Solid State **49**, 443 (2007).
11. Y. Akishige, Y. Yamamoto, K. Ohi. Jap. J. Appl. Phys. **21**, 1037 (1982).
12. S.Y. Wu, H.N. Dong, W.H. Wei. Z.Naturforsch. **59a**, 203 (2004).
13. V.V.Laguta, M.D.Glinchuk, A.A.Karmazin, I.P.Bykov. Physics of the Solid State **27**, 162 (1985).
14. I.P.Bykov, M.D.Glinchuk, A.A.Karmazin, V.V.Laguta. Physics of the Solid State **25**, 3586 (1983).